

## Research Article

# Conformational Analysis of Quaternary Ammonium-Type Ionic Liquid Cation, *N,N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl) Ammonium Cation

Takahiro Takekiyo,<sup>1</sup> Yusuke Imai,<sup>2</sup> Hiroshi Abe,<sup>2</sup> and Yukihiro Yoshimura<sup>1</sup>

<sup>1</sup> Department of Applied Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan

<sup>2</sup> Department of Materials Science and Engineering, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan

Correspondence should be addressed to Takahiro Takekiyo, take214@nda.ac.jp

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Conformational preference of *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium cation ([DEME]<sup>+</sup>), which is one of the quaternary ammonium-based ionic liquid cation, in the gas phase has been investigated using a density functional theory (DFT) calculation. Eight candidates for the stable conformers of [DEME]<sup>+</sup> exist in the gas phase, and can be energetically classified into two groups. One is a five conformers group, which has the N<sup>+</sup> ··· O<sup>-</sup> intramolecular attractive interaction form (the folded form). The other is a three conformers group, which is the noninteraction form (the extended form). The transformation from the folded form to the extended form induces large changes in the dipole moment and partial charges of N and O atoms. Here we show that the difference in the dipole moment and partial charges of N and O atoms associated with the conformational change of [DEME]<sup>+</sup> are closely related to the molecular orientation of [DEME]-based ionic liquids in the liquid state.

## 1. Introduction

The conformational analysis of room temperature ionic liquids (RTILs) using a vibrational spectroscopy combined with the quantum chemical calculation has been studied because the investigation of the conformational equilibria in RTILs is a good indicator of the molecular orientation for the phase transition and solution structure of RTILs [1–3].

Recently, the phase behaviors and solution structures of *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate ([DEME][BF<sub>4</sub>]) and iodide ([DEME][I]), which are typical quaternary ammonium-based RTILs, in the pure solution and also in the aqueous solutions have been investigated using various experimental techniques such as Raman, differential thermal analysis (DTA), and X-ray diffraction methods [4–12]. Imai et al. [4] and Abe et al. [8] reported the phase diagram of [DEME][BF<sub>4</sub>]-water mixed solutions as functions of temperature and water concentration. They found that [DEME][BF<sub>4</sub>]-water

mixed solutions show complicated phase behavior. Moreover, Yoshimura et al. [7] found the existence of the nearly free hydrogen bonds of water in the [DEME][BF<sub>4</sub>]-water mixed solutions at 298 and 77 K using a Raman spectroscopy. In this relation, Imai et al. [9, 12] reported that [DEME][X] (X = BF<sub>4</sub> and I)-water mixed solutions have double glass transition temperatures (*T<sub>g</sub>*) due to the liquid-liquid immiscibility using a DTA method. It is, however, still unclear the relationship between the molecular orientation such as conformation and the complicated phase behavior in the aqueous [DEME][X] (X = BF<sub>4</sub> and I) solutions.

Although the conformations of 1-alkyl-3-methylimidazolium-based RTILs have been well studied [2, 3, 13–18], there has been no report on the conformation of [DEME]<sup>+</sup>. As one of the reasons, many free internal rotations in the [DEME]<sup>+</sup> complicates the conformation of [DEME]<sup>+</sup> in the liquid states rather than those of 1-ethyl-3-methylimidazolium cation ([emim]<sup>+</sup>) and 1-butyl-3-methylimidazolium cation ([bmim]<sup>+</sup>). Clear identification of

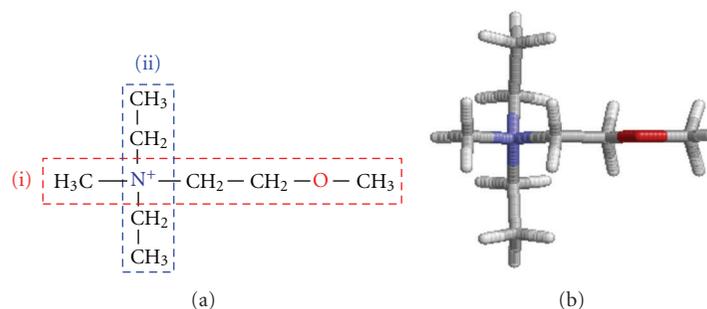


FIGURE 1: (a) Chemical and (b) optimized structures of [DEME]<sup>+</sup> using the B3LYP/6-311++G(d,p) basis set.

the stable conformers of [DEME]<sup>+</sup> in the liquid state is difficult, but, as a first step, it is important to reveal the stable conformers of [DEME]<sup>+</sup> in the gas phase for determining the complicated conformation in the liquid state.

In this study, we have attempted to determine the conformational preference of [DEME]<sup>+</sup> in the gas phase using a density functional theory (DFT) calculation. Our calculation results show that [DEME]<sup>+</sup> in the isolated system classifies into the N<sup>+</sup> ··· O<sup>-</sup> intramolecular attractive interaction form (the folded form) and the noninteraction form (the extended form). These forms have large differences in the dipole moments and partial charges.

## 2. Experimental

Density functional theory (DFT) calculations were carried out using GAUSSIAN03 program [19]. For the present calculation of [DEME]<sup>+</sup>, we used the Becke's three-parameter (B3) exchange function [20]. The B3 exchange function was combined with Lee-Yang-Pear correlation function (B3LYP) [21]. Calculations of geometries, total energies, and atomic charges of [DEME]<sup>+</sup> were performed using the 6-311++G(d,p) basis set. The normal coordinate calculations using the B3LYP method were performed by uniform wavenumber scaling factor ( $f$ ) of 0.9613. The basis set superposition errors (BSSEs) were confirmed to be negligible by the counterpoise method [22, 23]. The initial structure of [DEME]<sup>+</sup> was started from the all *trans* conformer shown in Figure 1. The Breneman and Wiberg CHELPG scheme [24, 25] was used to determine the atomic charges from the electrostatic potentials.

## 3. Results and Discussion

We consider the conformations on (i) the CN<sup>+</sup>CCOC chain and (ii) the ethyl-chain (CCN<sup>+</sup>C) to determine the conformational preference of [DEME]<sup>+</sup>. First, we focused on the conformational preference of the CN<sup>+</sup>CCO<sup>-</sup>C chain. The changes in potential energy surfaces (PES) for the CN<sup>+</sup>CC, N<sup>+</sup>CCO<sup>-</sup>, and CCO<sup>-</sup>C angles were performed by the B3LYP/6-311++G(d,p) basis set as shown in Figure 2. As seen in Figure 2(a), the CN<sup>+</sup>CC angle has double energy minima at  $\pm 30^\circ$ . The energy differences ( $\Delta E$ ) between at  $\pm 180^\circ$  and  $\pm 30^\circ$  of the CN<sup>+</sup>CC angle showed a large value (over +20 kJ mol<sup>-1</sup>). The CN<sup>+</sup>CC angle energetically prefers to the angle at  $180^\circ$  (the *trans* form). A remarkable result is

the change in the PES for the N<sup>+</sup>CCO<sup>-</sup> angle. The N<sup>+</sup>CCO<sup>-</sup> angle showed the smallest PES change among three angles, and has double energy minima at  $\pm 85^\circ$ .  $\Delta E$  between at  $\pm 180^\circ$  and  $\pm 85^\circ$  (the *gauche*<sup>±</sup> form) of the N<sup>+</sup>CCO<sup>-</sup> angle are about -1.3 kJ/mol, and are below a  $RT$  order (2.48 kJ/mol). The N<sup>+</sup>CCO<sup>-</sup> angle takes the *trans* form ( $180^\circ$ ) and the *gauche*<sup>±</sup> form ( $\pm 85^\circ$ ), and the *gauche*<sup>±</sup> form is energetically more stable than the *trans* form. On the other hand, the CCO<sup>-</sup>C angle having the nonenergy minimum only takes the *trans* form because the PES shows the lowest at  $180^\circ$ . On the basis of these results, the CN<sup>+</sup>CC and N<sup>+</sup>CCO<sup>-</sup> angles may be important key to determine the conformation of the CN<sup>+</sup>CCO<sup>-</sup>C chain. Therefore, the CN<sup>+</sup>CCO<sup>-</sup>C chain takes the *trans-trans-trans* (*ttt*) and *trans-gauche-trans* (*tgt*) conformers.

Here, we must discuss why the *gauche*<sup>±</sup> form of the N<sup>+</sup>CCO<sup>-</sup> angle is stable. One possible explanation is the electron polarizabilities of N and O atoms. According to the DFT and Raman studies by Yoshida et al. [26, 27], the OCCO angle of 1,2-dimethoxyethane (DME: CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>) prefers the *gauche* form to the *trans* form owing to the electron polarizability of O atoms. Thus, we presume that the higher stability of the *gauche*<sup>±</sup> form for the N<sup>+</sup>CCO<sup>-</sup> angle of [DEME]<sup>+</sup> might arise from the intramolecular attractive interaction due to the electron polarizabilities of N and O atoms because the structure of N<sup>+</sup>COO<sup>-</sup> angle of [DEME]<sup>+</sup> resembles that of the OCCO angle of DME.

To assess this speculation, we estimated the partial atomic charges ( $\delta_N$  and  $\delta_O$ ) of the N and O atoms, the distance ( $d_{N\dots O}$ ) between the N and O atoms, and dipole moment ( $\mu$ ) for the [DEME]<sup>+</sup> conformers using the B3LYP/6-311++G(d,p) basis set. When the N<sup>+</sup>CCO<sup>-</sup> angle takes the *trans* form, the  $\delta_N$  and  $\delta_O$  values are +0.19 and -0.40, respectively, and the  $d_{N\dots O}$  and  $\mu$  values are 3.72 Å and 4.12 D, respectively. On the other hand, when the N<sup>+</sup>CCO<sup>-</sup> angle takes the *gauche*<sup>±</sup> form, the  $\delta_N$  and  $\delta_O$  values are about +0.12 and -0.30, respectively, and the  $d_{N\dots O}$  and  $\mu$  values 3.06 Å, and 2.67 D. Thus, with transforming from the *trans* to *gauche*<sup>±</sup> forms, the  $\delta_N$  and  $\delta_O$  values become smaller and the value of  $d_{N\dots O}$  becomes shorter. The  $\mu$  value becomes larger ( $\Delta\mu^{\text{trans-gauche}} = 1.45$  D). Accordingly, we conclude that the intramolecular attractive interaction due from the electron polarizabilities of N and O atoms is the main cause for the higher *gauche* stability of the N<sup>+</sup>CCO<sup>-</sup> angle of [DEME]<sup>+</sup>.

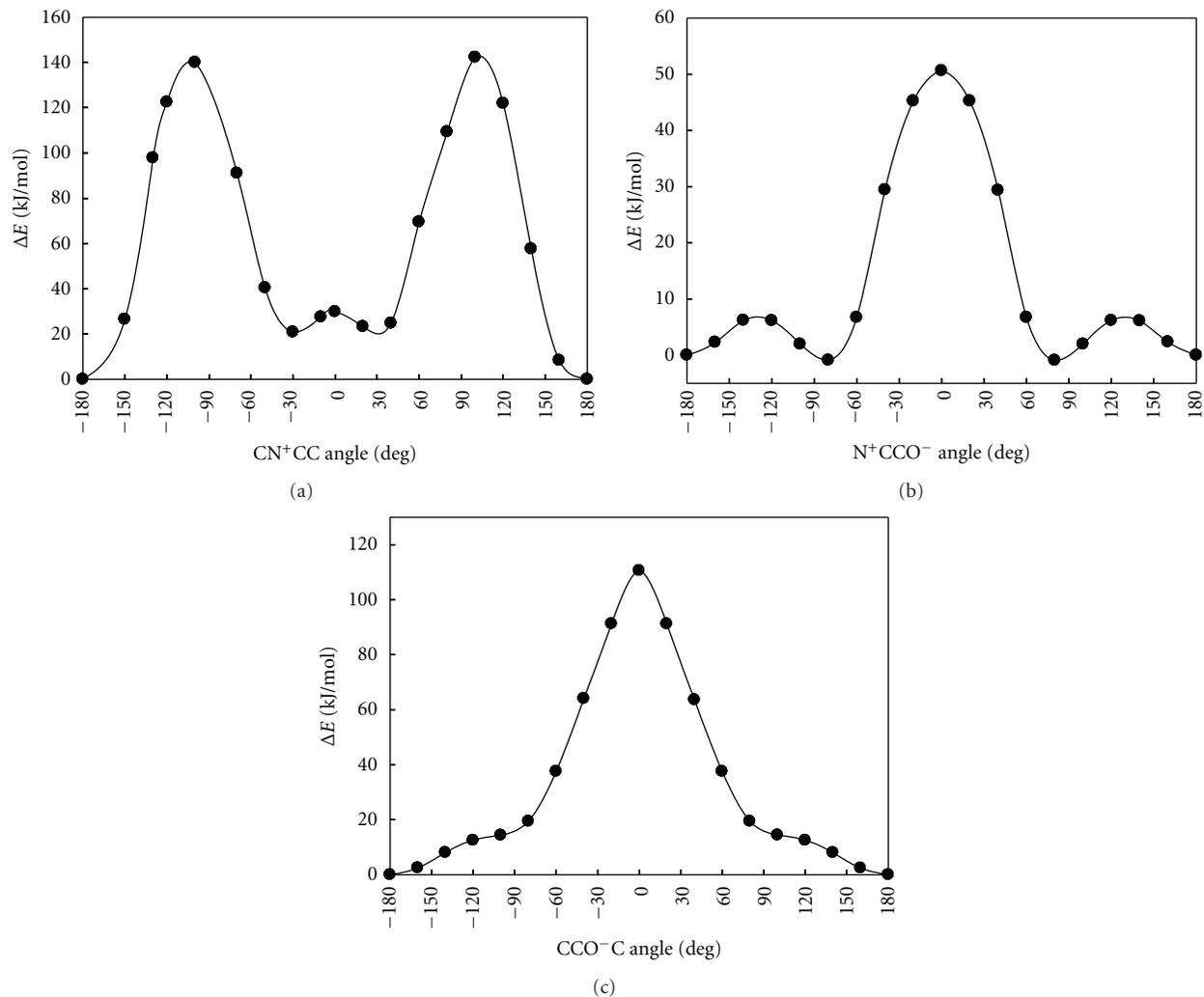


FIGURE 2: Potential energy surface of the side chain of [DEME]<sup>+</sup> as a function of (a) CN<sup>+</sup>CC, (b) N<sup>+</sup>CCO<sup>-</sup>, and (c) CCO<sup>-</sup>C dihedral angles. Here, two CCN<sup>+</sup>C angles for the ethyl-group of [DEME]<sup>+</sup> are fixed at 180°, whose angle corresponds to *trans* form.

TABLE 1: Energy difference ( $\Delta E$ ) between the ethyl-chain conformers of [DEME]<sup>+</sup> cation.

Conformer	$\Delta E^{TT-XX}$ (kJ/mol)
<i>TT</i>	0
<i>TG</i> <sup>+</sup>	+2.24
<i>TG</i> <sup>-</sup>	+13.0
<i>G</i> <sup>-</sup> <i>G</i> <sup>-</sup>	+13.4
<i>G</i> <sup>-</sup> <i>G</i> <sup>+</sup>	+16.6
<i>G</i> <sup>+</sup> <i>G</i> <sup>-</sup>	+16.8
<i>G</i> <sup>+</sup> <i>G</i> <sup>+</sup>	+26.2

Next, we must consider an affection from the ethyl-chain for the conformational stability of the CN<sup>+</sup>CCO<sup>-</sup>C chain since the steric effect owing to the conformational preference of ethyl-chain group would change the conformational stability of the CN<sup>+</sup>CCO<sup>-</sup>C chain. In an effort to ensure the affection from the ethyl-chain for the conformational

stability of the CN<sup>+</sup>CCO<sup>-</sup>C chain, we calculated the PES of CCN<sup>+</sup>C dihedral angles of the ethyl-chain. Seven conformers of ethyl-chain are found to be energetically stable; the *TT*, *TG*<sup>+</sup>, *TG*<sup>-</sup>, *G*<sup>-</sup>*G*<sup>-</sup>, *G*<sup>-</sup>*G*<sup>+</sup>, *G*<sup>+</sup>*G*<sup>-</sup>, and *G*<sup>+</sup>*G*<sup>+</sup> conformers. Here, the large letters of “*T*”, “*G*<sup>+</sup>”, and “*G*<sup>-</sup>” represent the *Trans*, *Gauche*<sup>+</sup> (+: the positive angle for the *gauche* form) and *Gauche*<sup>-</sup> (-: the negative angle for the *gauche* form) forms, respectively. From the results of  $\Delta E^{TT-XX}$  ( $XX = TG^+, TG^-, G^-G^-, G^-G^+, G^+G^-,$  and  $G^+G^+$ ) as shown in Table 1, the *TT* and *TG*<sup>+</sup> conformers have higher energetic stability rather than other conformers. Previous quantum chemistry calculations indicated that the *gauche* form of tetraethylammonium cation (Et<sub>4</sub>N<sup>+</sup>) having the similar structure of [DEME]<sup>+</sup> is less stable than the *trans* form due to the steric effect in the gas phase [28, 29]. The energy calculation of the ethyl-chain conformers of [DEME]<sup>+</sup> qualitatively agrees with the quantum chemistry calculation results of Et<sub>4</sub>N<sup>+</sup> [28, 29].

We checked the conformational preference of the CN<sup>+</sup>CCO<sup>-</sup>C chain again, when the ethyl-chain takes

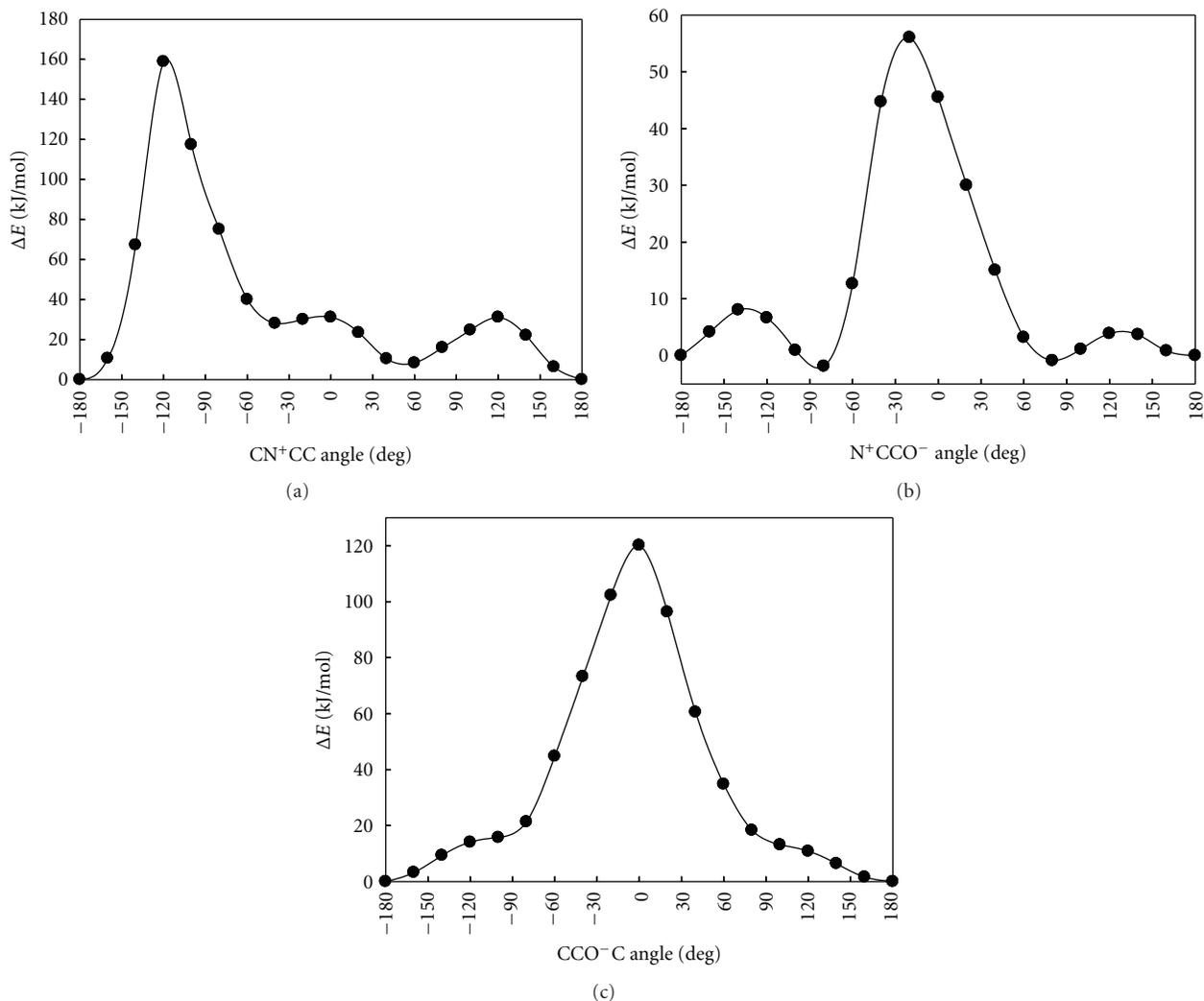
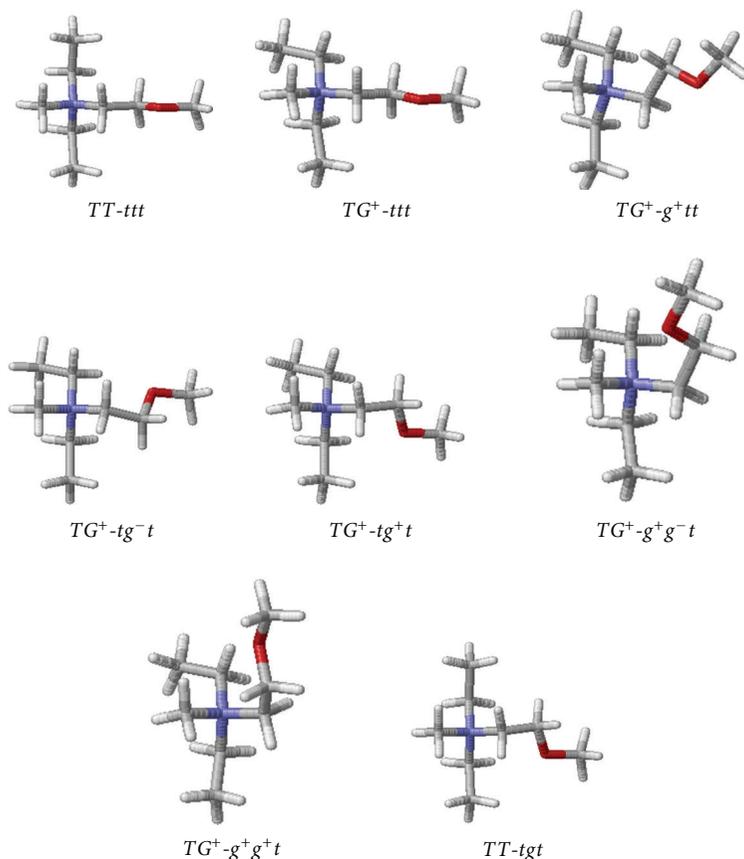


FIGURE 3: Potential energy surface of the side chain of [DEME]<sup>+</sup> as a function of (a)  $\text{CN}^+\text{CC}$ , (b)  $\text{N}^+\text{CCO}^-$ , and (c)  $\text{CCO}^- \text{C}$  dihedral angles when the ethyl-chain takes the *TG*<sup>+</sup> conformer.

the *TG*<sup>+</sup> conformer (Figure 3). Compared with Figures 2 and 3, the stable conformers of the  $\text{N}^+\text{CCO}^-$  and  $\text{CCO}^- \text{C}$  angles are independent of the ethyl-chain conformers. On the other hand, the change in the PES of  $\text{CN}^+\text{CC}$  angle is largely dependent of the ethyl-chain conformers since the position of the  $\text{CN}^+\text{CC}$  angle is very close with the ethyl-chain. Thus, transformation from the *TT* conformer to *TG*<sup>+</sup> conformer of the ethyl-chain causes the change in double energy minima of the  $\text{CN}^+\text{CC}$  angle. Especially, the energy minimum of the  $\text{CN}^+\text{CC}$  angle at +30° moved to the angle at +60° (the *gauche* form) by a steric effect between the ethyl-chain and the  $\text{CN}^+\text{CCO}^- \text{C}$  chain, and  $\Delta E$  between at 180° and +60° for the  $\text{CN}^+\text{CC}$  angle is +8.6 kJ/mol. The *gauche*<sup>+</sup> and *trans* forms of  $\text{CN}^+\text{CC}$  angle are energetically stable when the ethyl-chain takes the *TG*<sup>+</sup> conformer. Therefore, when the  $\text{CN}^+\text{CC}$  angle takes the *TG*<sup>+</sup> conformer, the  $\text{CN}^+\text{CCO}^- \text{C}$  chain takes the six conformers; the *tg*<sup>+</sup>*t*, *tg*<sup>-</sup>*t*, *ttt*, *g*<sup>+</sup>*g*<sup>+</sup>*t*, *g*<sup>+</sup>*g*<sup>-</sup>*t*, and *g*<sup>+</sup>*tt* conformers, respectively.

In view of the results from the conformational combinations of the  $\text{CN}^+\text{CCO}^- \text{C}$  chain and ethyl-chain,

[DEME]<sup>+</sup> can take eight conformers in the gas phase as shown in Figure 4. The energy difference and structural parameters for eight conformers of [DEME]<sup>+</sup> were done as shown in Table 2. The rank ordering of the conformational stability of [DEME]<sup>+</sup> is *TT-tgt* > *TG*<sup>+</sup>-*g*<sup>+</sup>*g*<sup>+</sup>*t* > *TG*<sup>+</sup>-*tg*<sup>+</sup>*t* > *TG*<sup>+</sup>-*g*<sup>+</sup>*g*<sup>-</sup>*t* > *TG*<sup>+</sup>-*tg*<sup>-</sup>*t*  $\gg$  *TT-ttt* > *TG*<sup>+</sup>-*ttt* > *TG*<sup>+</sup>-*g*<sup>+</sup>*tt*. (Here the large and small letters (*XX-xxx*) represent the conformers for the ethyl-chain (*XX*) and the  $\text{CN}^+\text{CCO}^- \text{C}$  chain (*xxx*), resp.) A notable point is the balance of  $\Delta E$  among the conformers. Eight conformers can energetically classify into two types. One is a group taking the *trans* form for the  $\text{N}^+\text{CCO}^-$  angle (*TT-ttt*, *TG*<sup>+</sup>-*ttt*, and *TG*<sup>+</sup>-*g*<sup>+</sup>*tt*). The other is a group taking the *gauche* form for the  $\text{N}^+\text{CCO}^-$  angle (*TT-tgt*, *TG*<sup>+</sup>-*g*<sup>+</sup>*g*<sup>+</sup>*t*, *TG*<sup>+</sup>-*tg*<sup>+</sup>*t*, *TG*<sup>+</sup>-*g*<sup>+</sup>*g*<sup>-</sup>*t*, and *TG*<sup>+</sup>-*tg*<sup>-</sup>*t*). Probably, the higher stability of five conformers results from the  $\text{N}^+ \cdots \text{O}^-$  intramolecular attractive interaction between the N and O atoms. Interestingly, this classification is independent on the ethyl-chain conformer. The former group structurally may be depicted as an extended form and the later group as a folded form. Therefore, [DEME]<sup>+</sup> in

FIGURE 4: Optimized eight conformers of  $[\text{DEME}]^+$  using the B3LYP/6-311++G(d,p) basis set.TABLE 2: Energy difference ( $\Delta E^{ttt-xxx}$ ), dihedral angles ( $\theta_{\text{CN}^+\text{CC}}$  and  $\theta_{\text{N}^+\text{CCO}^-}$ ), and distance between N and O atoms ( $d_{(\text{N}\dots\text{O})}$ ). Partial charges ( $\delta^{\text{N}}$  and  $\delta^{\text{O}}$ ) of N and O atoms, and dipole moment ( $\mu$ ) of each conformer of  $[\text{DEME}]^+$  ion using the B3LYP/6-311++G(d,p) basis set.

Conformer	$\Delta E^{ttt-xxx}$ (kJ/mol)	$\theta_{\text{CN}^+\text{CC}}$ (degree)	$\theta_{\text{N}^+\text{CCO}^-}$ (degree)	$d_{(\text{N}\dots\text{O})}$ ( $\text{\AA}$ )	$\delta_{\text{N}}$	$\delta_{\text{O}}$	$\mu$ (Debye)
<i>TT</i> conformer							
<i>ttt</i>	0	179.98	179.98	3.72	0.19	-0.41	4.12
<i>tg<sup>+</sup>t</i>	-13.08	172.26	64.26	3.06	0.11	-0.25	2.67
<i>tg<sup>-</sup>t</i>	-13.08	172.21	-64.34	3.06	0.11	-0.25	2.67
<i>TG</i> conformer							
<i>ttt</i>	0	179.34	172.24	3.72	0.19	-0.38	3.77
<i>g<sup>+</sup>tt</i>	+1.56	66.24	168.53	3.72	0.19	-0.39	3.68
<i>tg<sup>+</sup>t</i>	-13.58	170.08	61.63	3.05	0.15	-0.27	2.67
<i>tg<sup>-</sup>t</i>	-12.91	167.31	-62.76	3.07	0.13	-0.33	2.45
<i>g<sup>+</sup>g<sup>+</sup>t</i>	-13.73	39.48	59.24	3.03	0.11	-0.27	2.13
<i>g<sup>+</sup>g<sup>-</sup>t</i>	-13.02	77.65	-57.92	3.01	0.10	-0.30	2.08

the isolated system has the intramolecular attractive interaction form (the folded form) and the noninteraction form (the extended form).

Another notable point is the difference in the average dipole moments of the folded and extended forms of  $[\text{DEME}]^+$ . Here, we mention the dipole moment ( $\mu$ ), which is expressed by the product of the total charges and distance between the positive and negative charges, of  $[\text{DEME}]^+$ .

$[\text{DEME}]^+$  is a monovalent cation but has a dipole moment ( $\mu$ ) due to the electron polarizabilities of N and O atoms in the  $\text{N}^+\text{CCO}^-$  chain. As mentioned above,  $[\text{DEME}]^+$  takes many conformers for the  $\text{N}^+\text{CCO}^-$  chain. Thus, the electron polarizabilities of N and O atoms and distance between the N and O atoms of each conformation are different as shown in Table 2. Consequently, each conformer has a different dipole moment ( $\mu = 2.13 \sim 4.12$  Debye (D))

despite that [DEME]<sup>+</sup> is a monovalent cation. According to previous calculation results, two conformers of other cations (e.g., [emim]<sup>+</sup> and [bmim]<sup>+</sup>) have a different dipole moment [15, 18]. The values of  $\mu$  for [emim]<sup>+</sup> are 1.13 D (planar) and 1.64 D (nonplanar), and those for [bmim]<sup>+</sup> are 5.76 D (*trans-trans*) and 4.96 D (*gauche-trans*), respectively. Interestingly, the  $\mu$  values of [DEME]<sup>+</sup> showed the same order with those of imidazolium cations.

The difference in the average dipole moments ( $\Delta\mu$ ) between the folded and extended forms is 1.45 D. The values of  $\Delta\mu$  between the planar and nonplanar conformers for [emim]<sup>+</sup> [15] and between the *trans-trans* and *gauche-trans* conformers of [bmim]<sup>+</sup> [18] are about 0.51 and 0.80 D, respectively.  $\Delta\mu$  among the conformers of [DEME]<sup>+</sup> obtained by the present calculation is larger than those of other imidazolium cations such as [emim]<sup>+</sup> and [bmim]<sup>+</sup>. This is clearly due to the electron polarizabilities of N and O atoms in the CN<sup>+</sup>CCO<sup>-</sup>C chain. Our calculation results indicated that the electron polarizabilities of the N and O atoms in the CN<sup>+</sup>CCO<sup>-</sup>C chain are the most important key for determining the intermolecular interaction between the [DEME]<sup>+</sup> and other molecular liquids or RTILs in the liquid state. In other words, the dipole moments and partial charges of N and O atoms associated with the conformational change of [DEME]<sup>+</sup> have close connection with various interesting phenomena such as complicated phase transitions, in [DEME][X] (X = BF<sub>4</sub> and I)-water mixed solutions [4–12].

Finally, we mention the relation of the present calculation of [DEME]<sup>+</sup> monomer in the gas phase and in the liquid state such as [DEME][X] (X = BF<sub>4</sub> and I). The average  $\Delta E$  between the folded and extended forms of [DEME]<sup>+</sup> is about 10 kJ/mol, and this energy corresponds to the energy of the hydrogen-bonded formation of molecules in the liquid state [30]. Therefore, the energy balance between the conformational equilibrium of [DEME]<sup>+</sup> in the liquid state may be different with that in the gas phase. It is known that interactions in RTILs are not weak, but strong and mostly electrostatic [31]. Actually some researchers have mentioned that around 50% to 15% of ions in RTILs exist as ion pairs [32, 33]. Thus, the conformation of [DEME]<sup>+</sup> in the liquid state is more complicated and the calculations might include larger size clusters such as ion pair, dimer.

In summary, conformational preference of [DEME]<sup>+</sup> in the *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium-based RTIL in the gas phase has been investigated by a DFT calculation. Present calculations showed that the [DEME]<sup>+</sup> consists of eight candidates for the conformers in the gas phase. We also found that [DEME]<sup>+</sup> has an equilibrium between the intramolecular attractive interaction form (the folded form) and the noninteraction form (the extended form) in the gas phase. We found that the CN<sup>+</sup>CCO<sup>-</sup>C chain is the most important key for determining the molecular orientation of [DEME]<sup>+</sup> in the liquid state. The present calculations determined the structural parameters and conformational identification of the complicated cation at the B3LYP level. Although a set of gas phase calculation on a single ion is simple, but this work may prove important to the community of force field developers. Further study such

as larger RTIL cluster size calculation including the ion pair and dimer may facilitate to understand more details of the complicated conformations of [DEME]<sup>+</sup> in the liquid state.

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